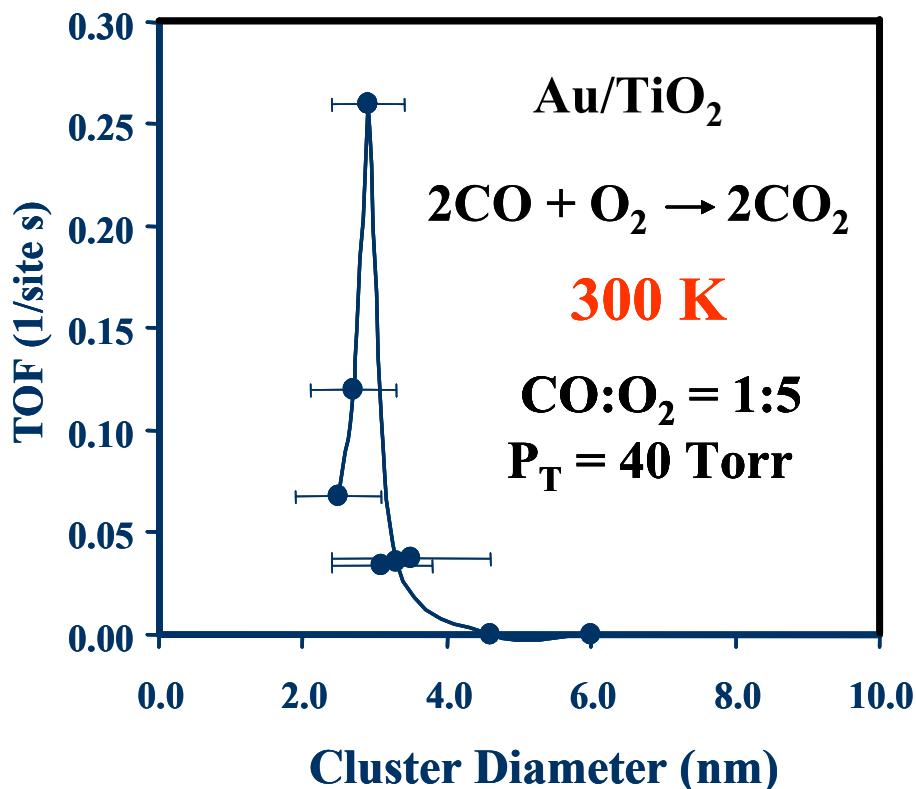


Catalysis by Supported Metal Nanoclusters: What's New?

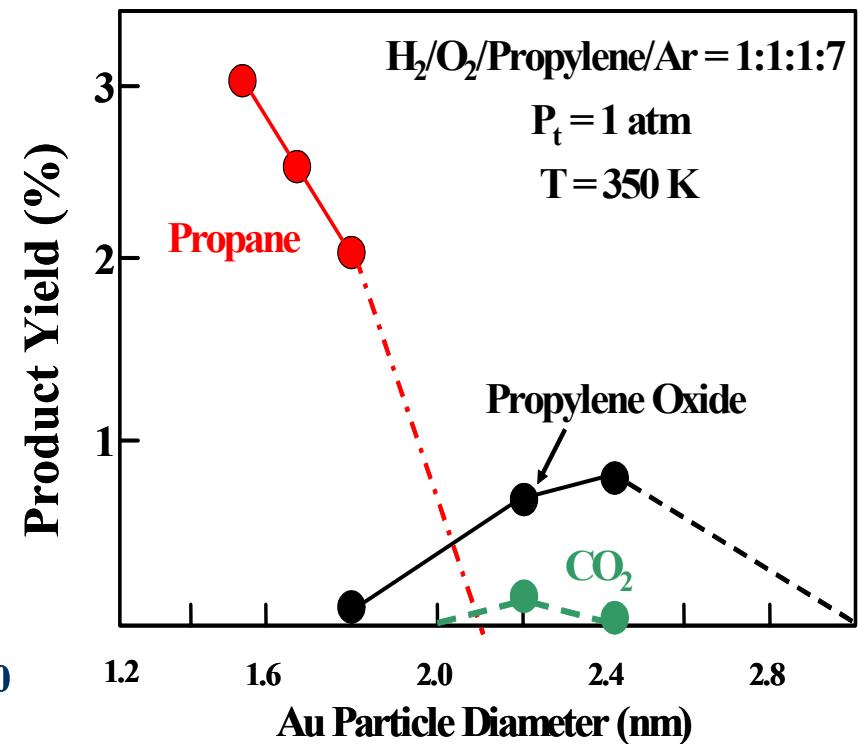
D. Wayne Goodman
Texas A&M University
Department of Chemistry

- Introduction to issues
- Special properties of metal nanoclusters
- Thermal stability of metal nanoclusters
- Strategies for designing sinter resistant catalysts
- How can neutrons help?

Unique Catalytic Activity of Nanosized Gold Particles

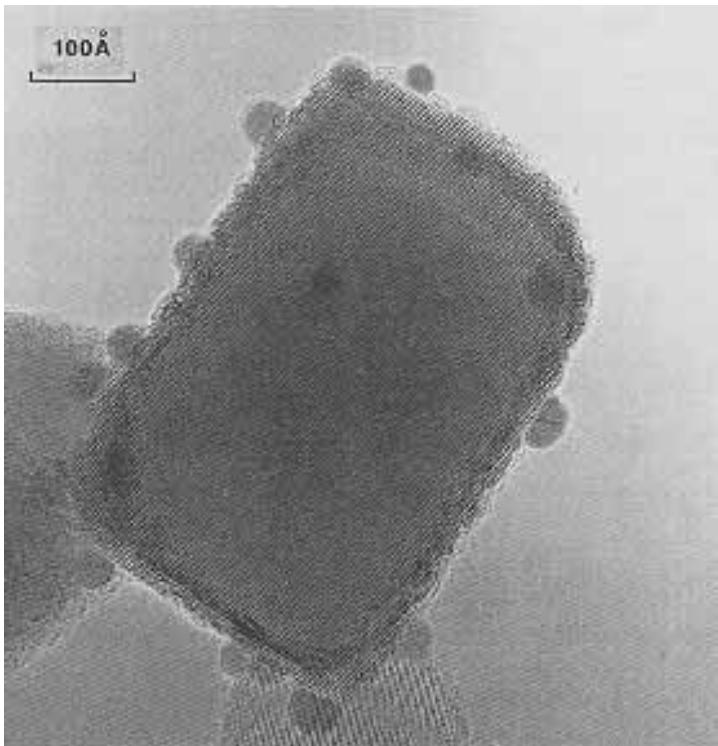


from Haruta, et al., Catalysis Letters (1997)

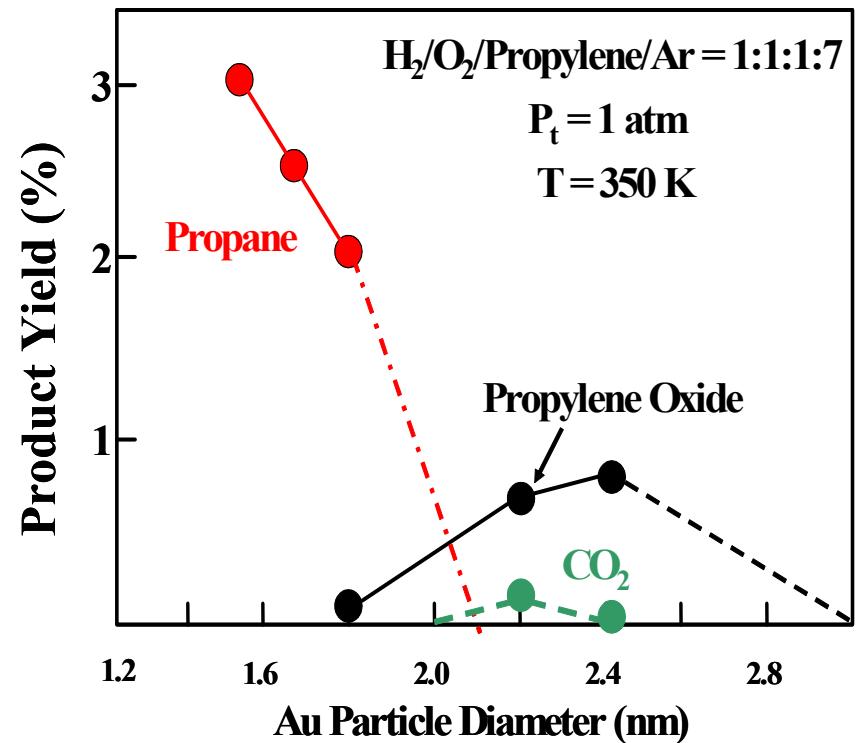


from Haruta, et al., Shokubai, Catalysts and Catalysis (1995)

Unique Catalytic Activity of Nanosized Gold Particles



TEM Image of Gold Supported on Titania (from M. Date, ONRI)



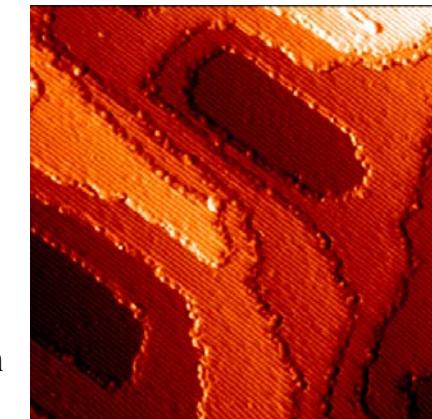
from Haruta, et al., Shokubai, Catalysts and Catalysis (1995)

Model Oxide-Supported Metal Catalysts

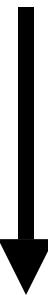
Single Crystal Oxide Support + Metal Clusters

e.g.
 TiO_2

Oxide Single Crystal



$\text{TiO}_2(110)$

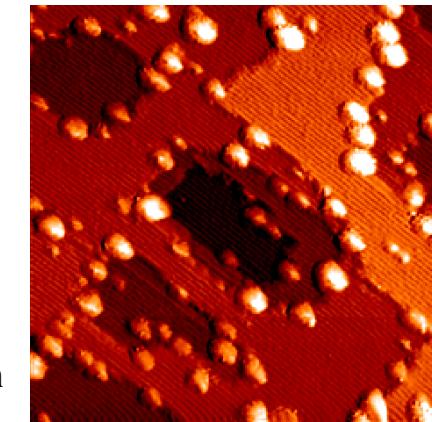


Metal Clusters
1.0-50 nm →

Oxide Single Crystal

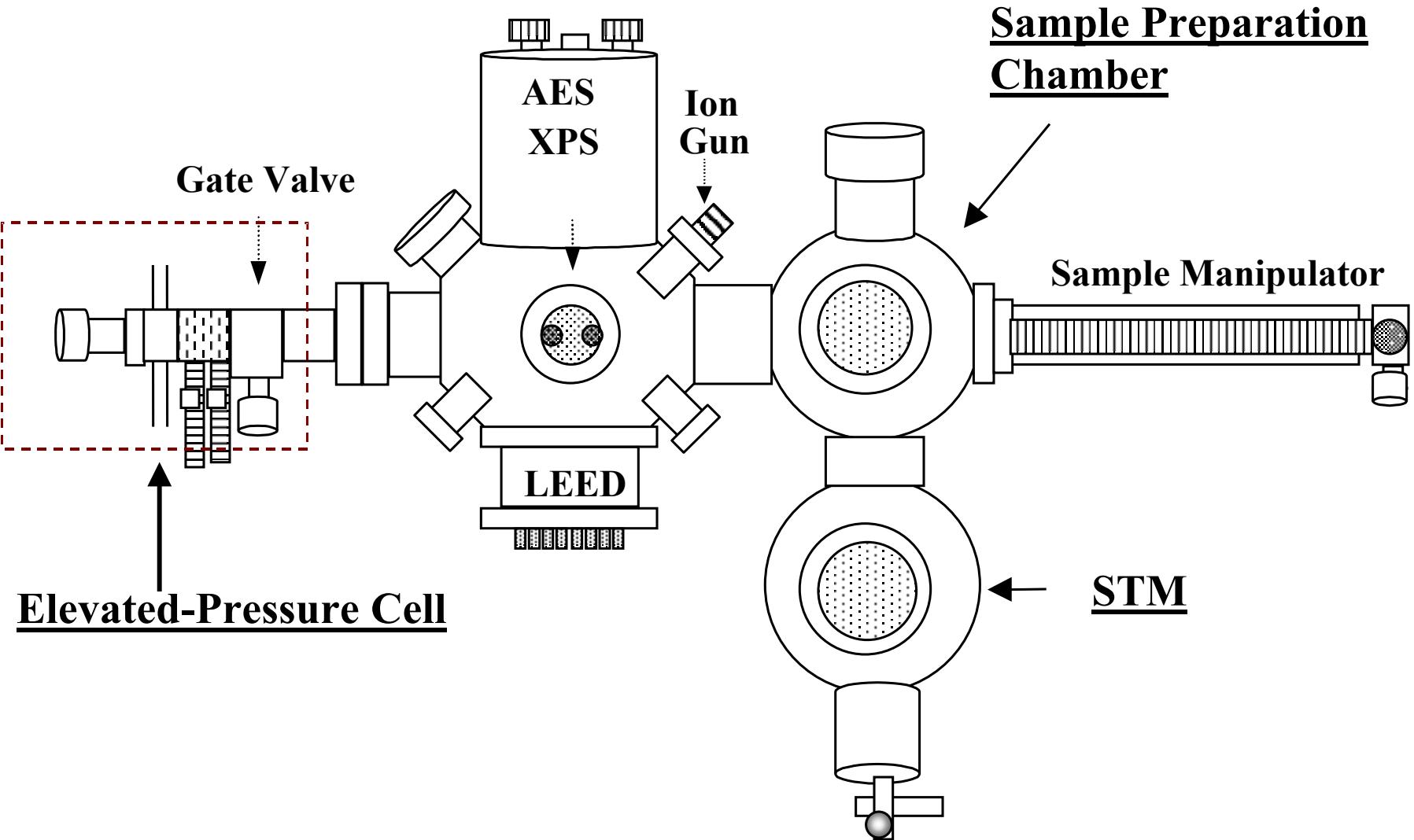


50 nm

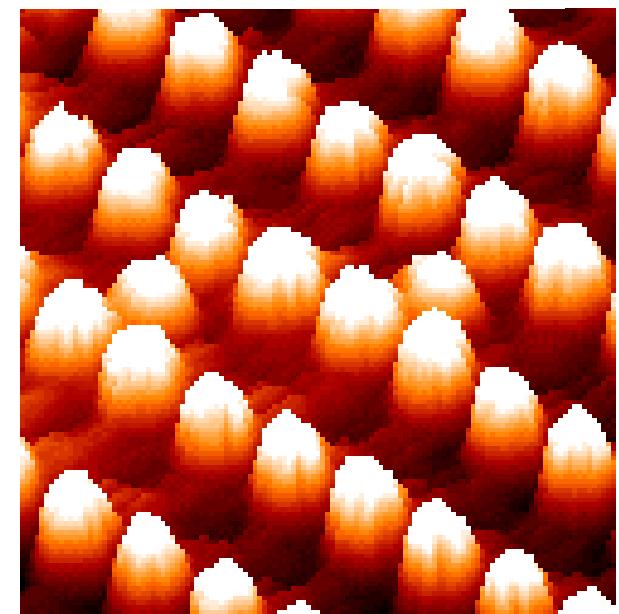
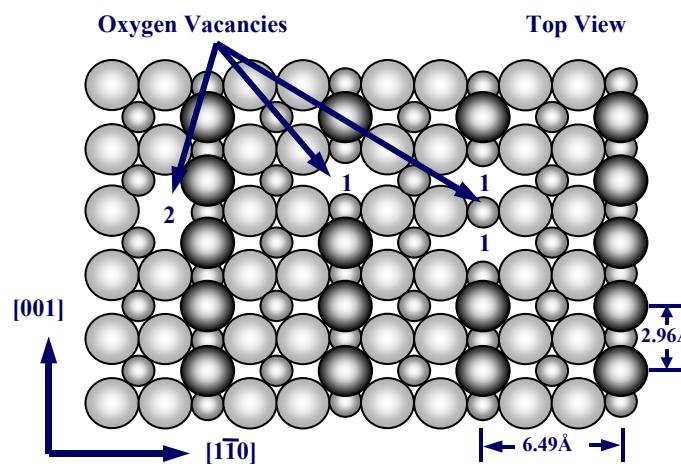
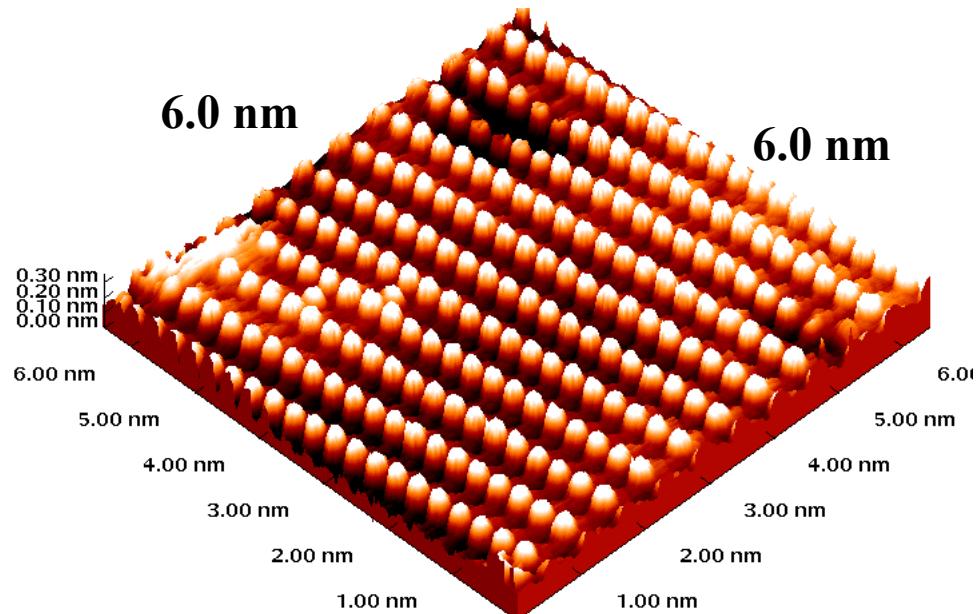
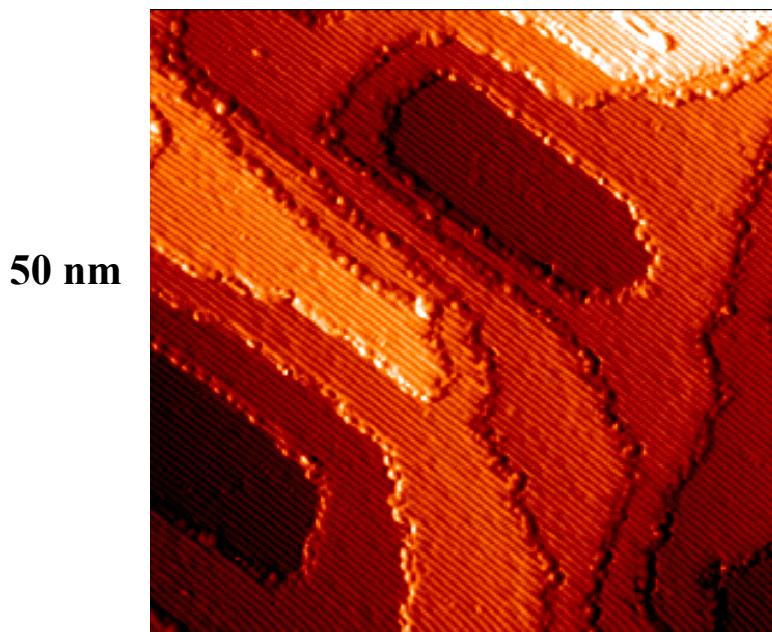


$\text{TiO}_2(110)$
+
0.25 Au

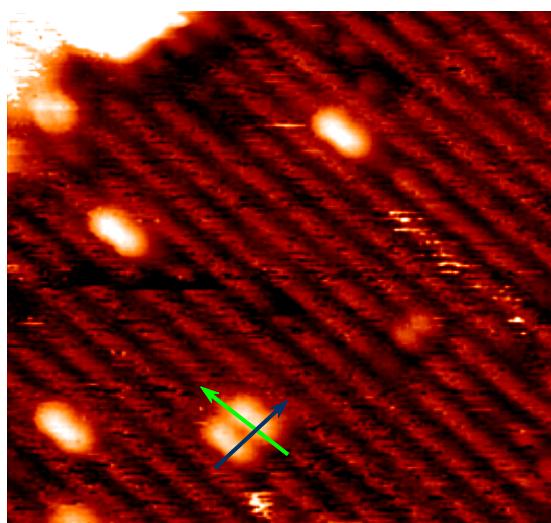
Apparatus



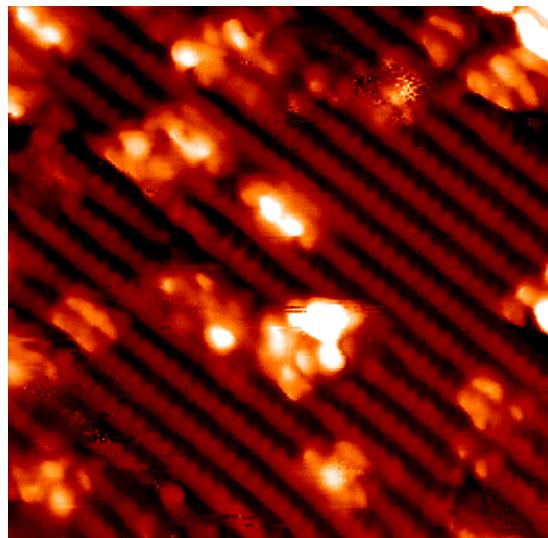
STM: $\text{TiO}_2(110)$



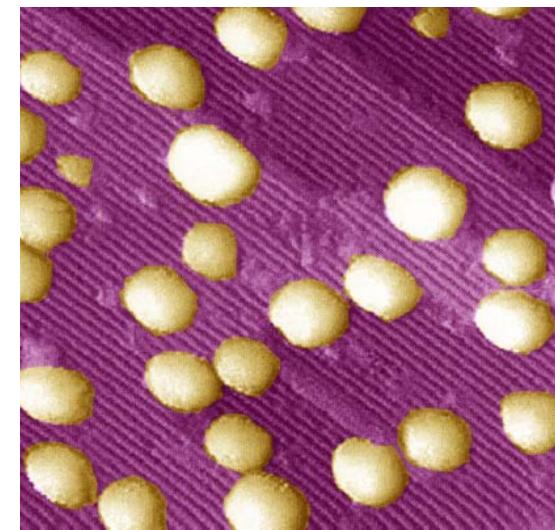
Morphology of Gold Clusters on TiO₂(110)



10 nm

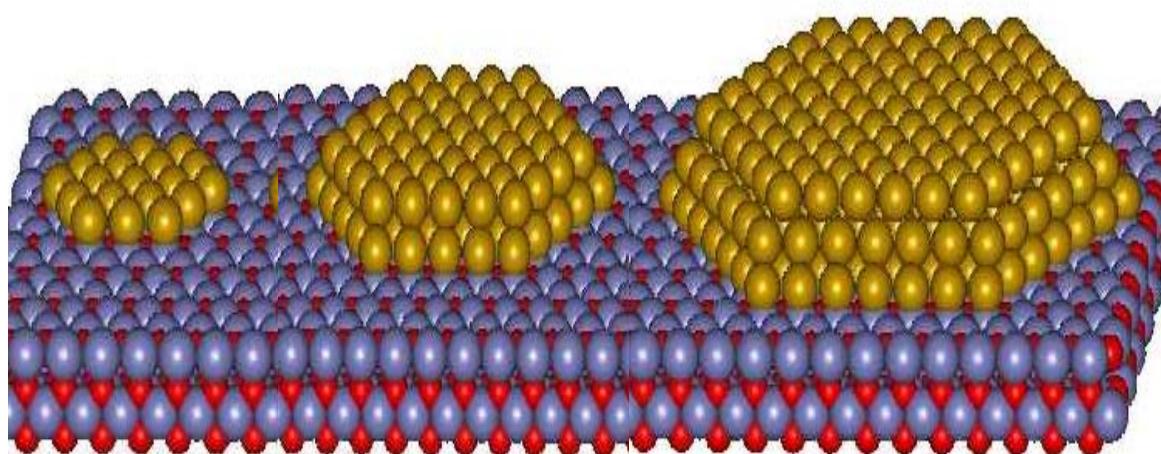


10 nm



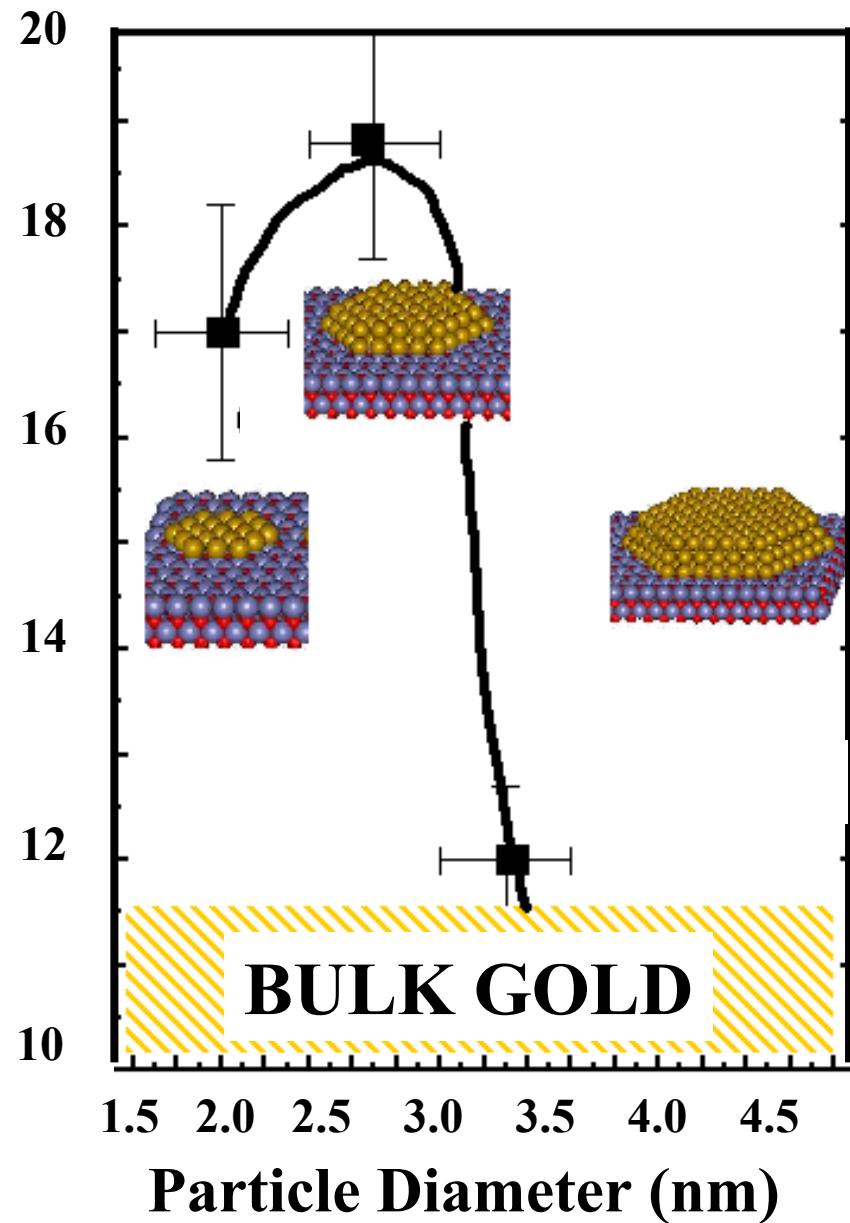
30 nm

INCREASING METAL CLUSTER SIZE



Isosteric Heats of CO Adsorption vs. Au Cluster Size

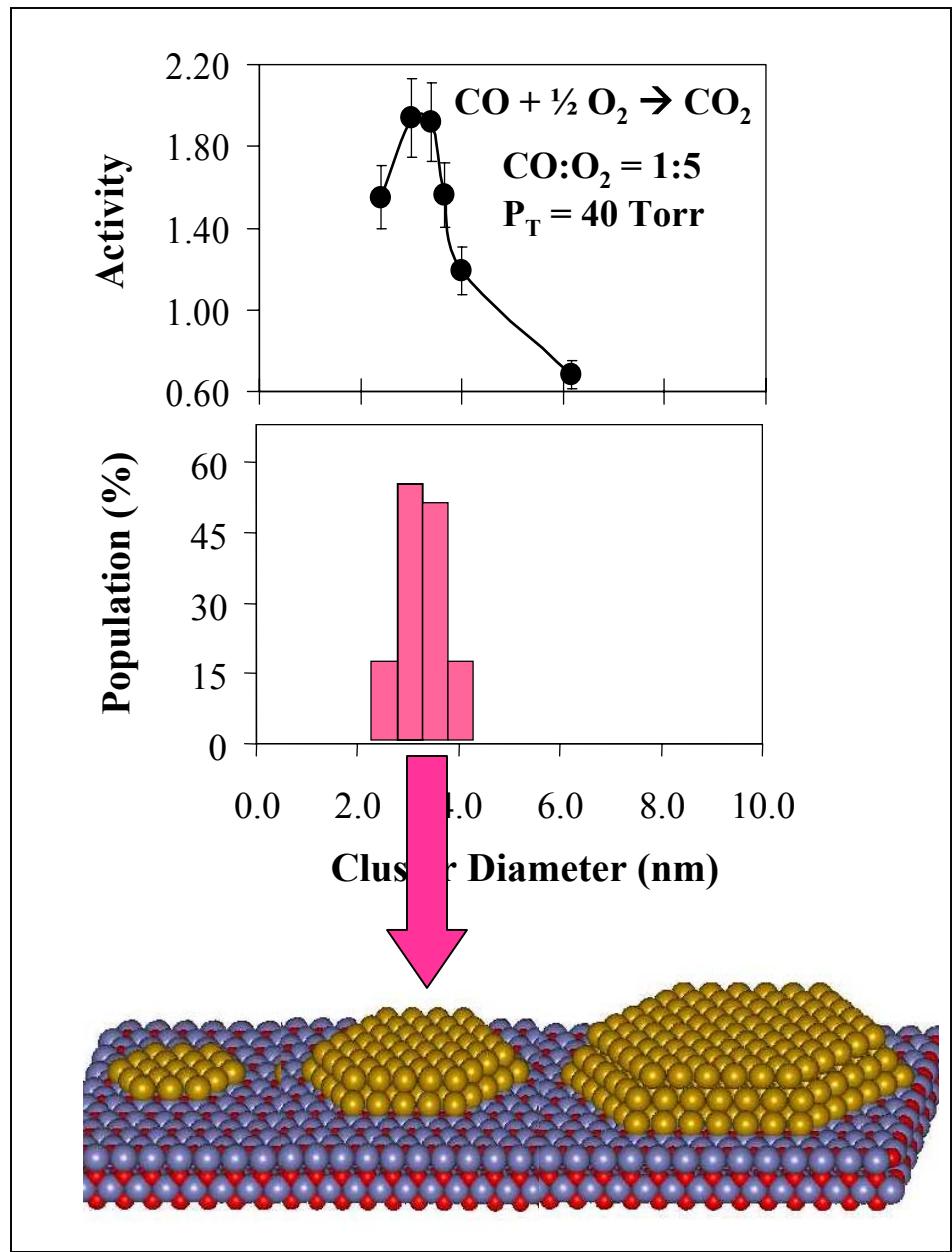
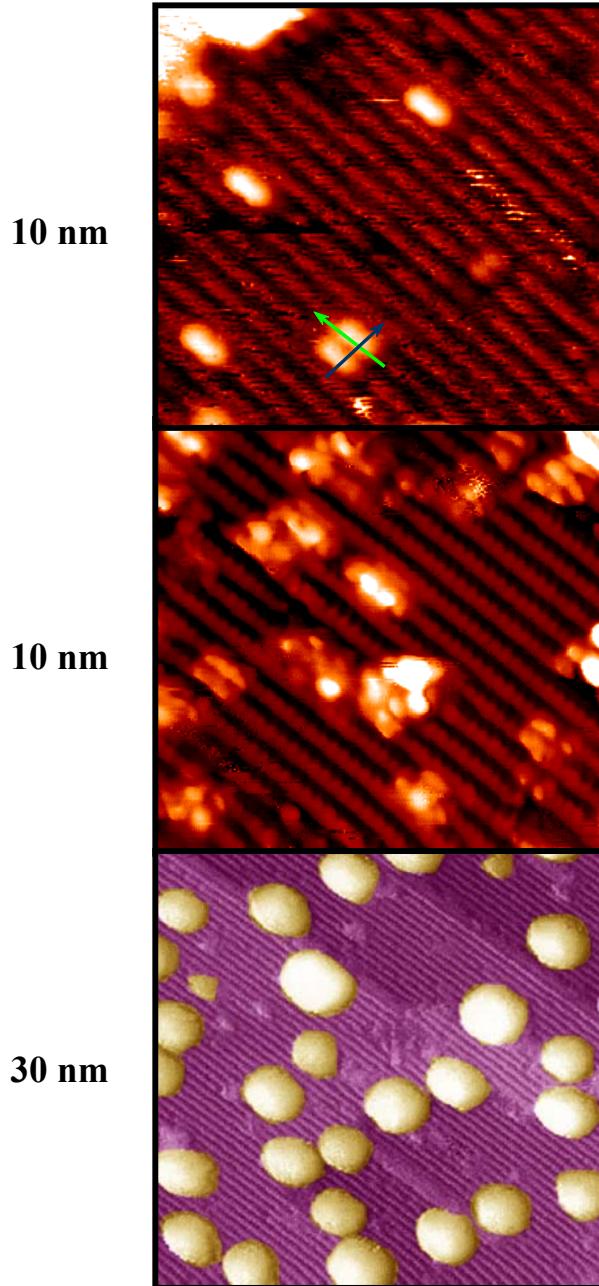
CO Heat of
Adsorption
(kcal/mol)



Clausius-Clapeyron
derived via
CO/IRAS at low
coverage limit

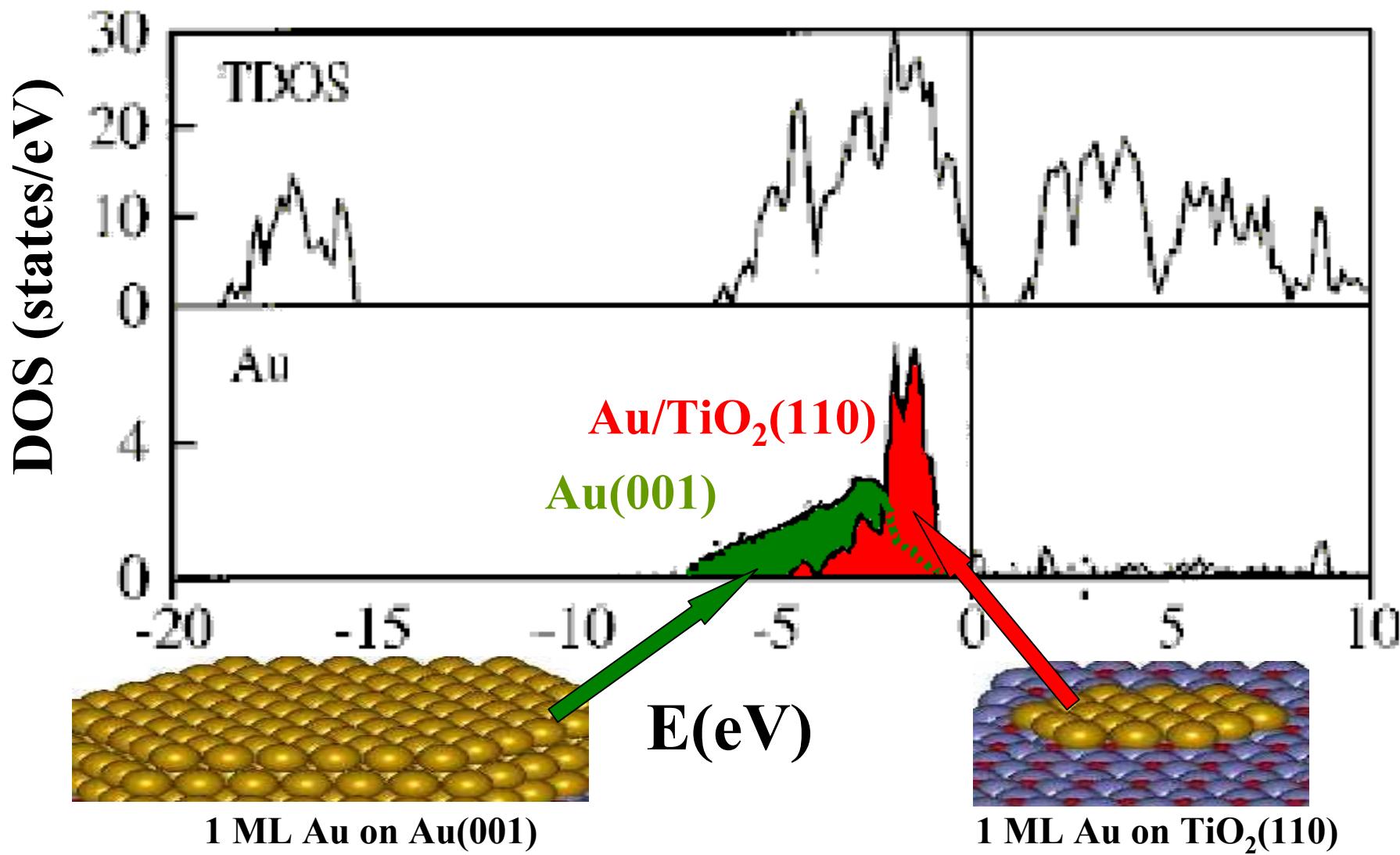
Meier, Bukhtiyarov, and
Goodman, J. Phys. Chem.,
(2003)

Effect of Cluster Size and Morphology on Reactivity of Au/TiO₂(110)



DFT Calculations for Au and Au/TiO₂(110)

Yang, Wu, Goodman, PRB (2000)

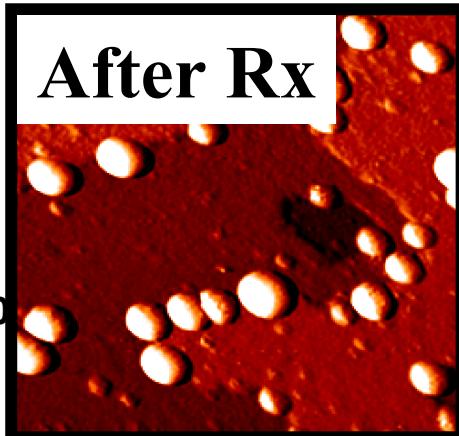
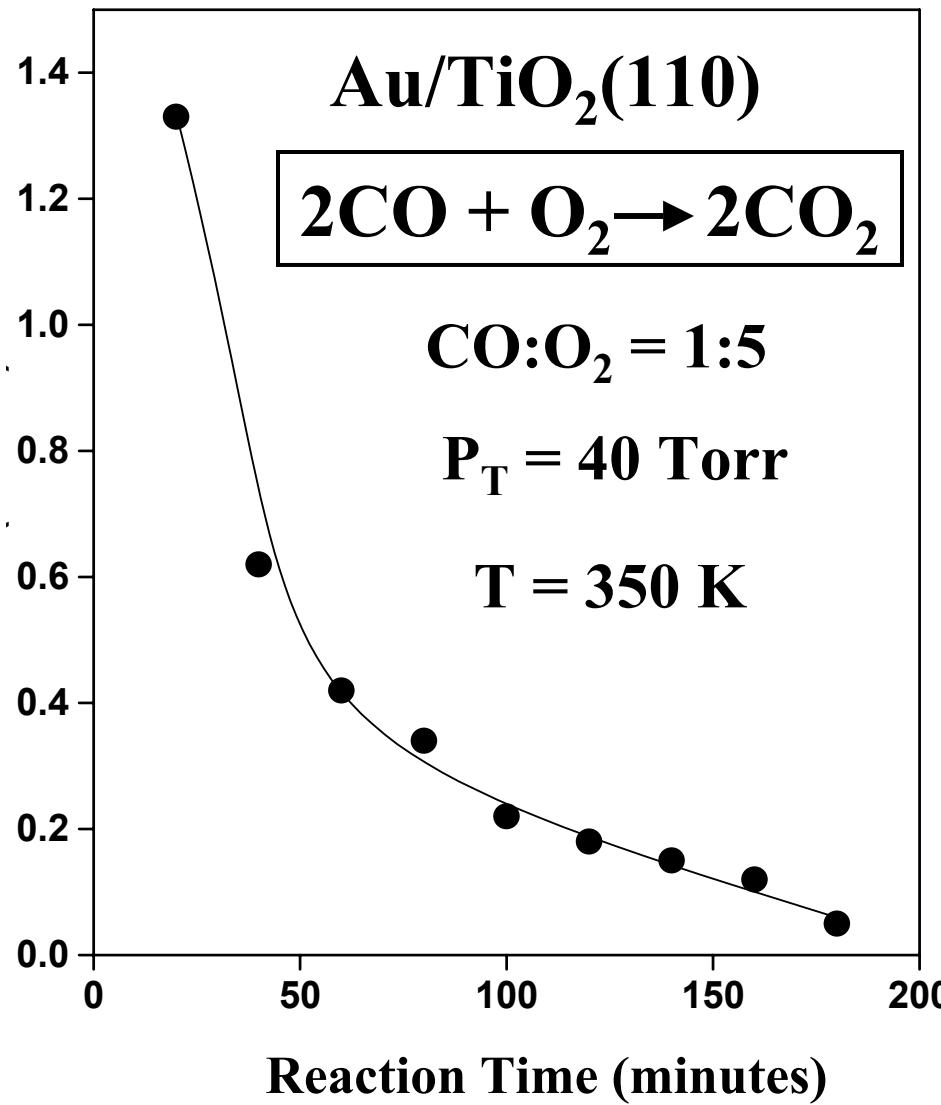


Summary: Properties of Supported Au Nanoclusters

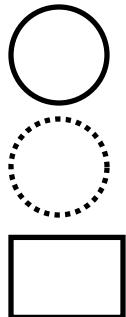
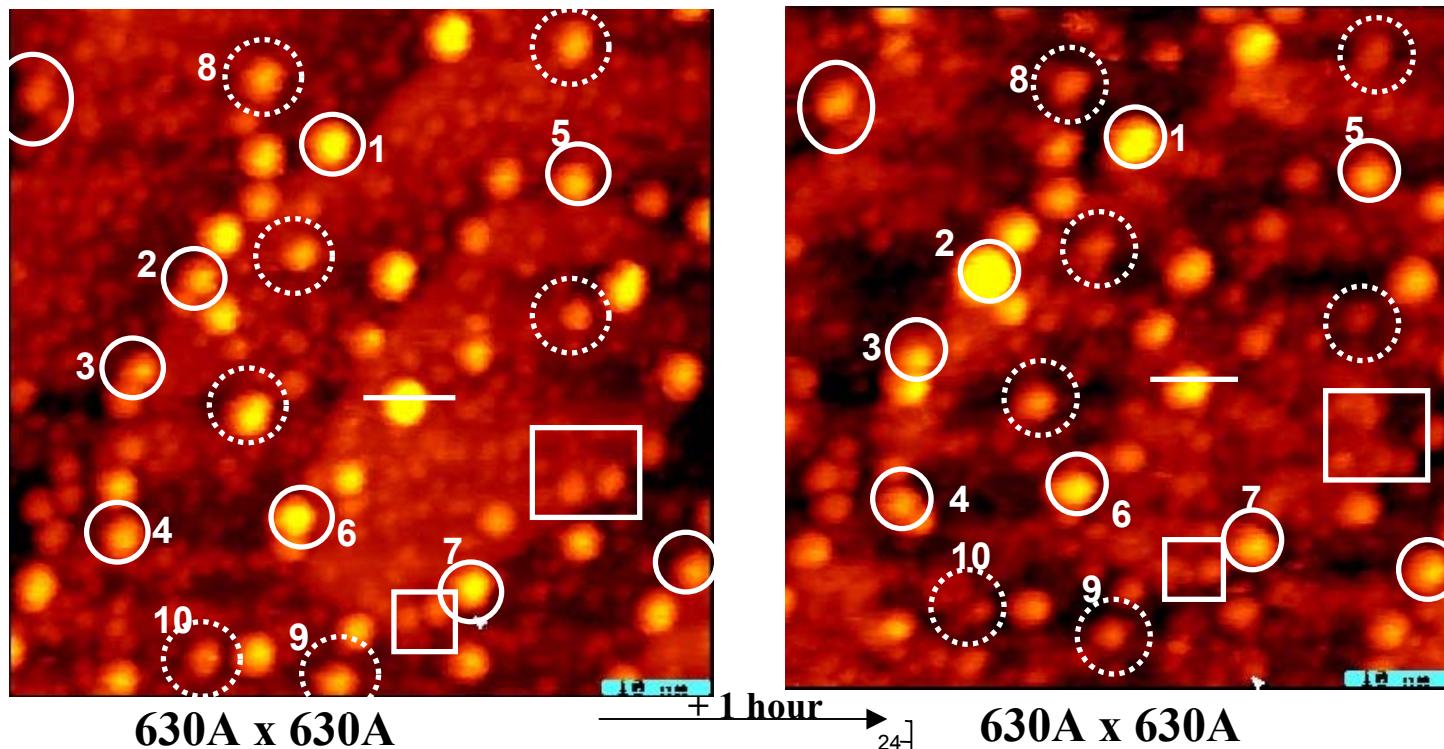
- Adsorbate binding energies, e.g. CO and O₂, change significantly from the bulk values for clusters < 3.0 nm.
- DFT calculations show center of Au d-band significantly destabilized for Au/TiO₂ compared to Au.
- Core-level shifts are markedly non-bulk-like at <ca. 3.0 nm.
- Surface plasmon not observed for clusters <ca. 3.0 nm.
- Sublimation energies of clusters < 3.0 nm are markedly lower than the corresponding bulk value.
- **Nanoclusters are generally unstable to reaction conditions, i.e., understanding and maintaining stability is a key to technological break-throughs.**

CO Oxidation Over Au/TiO₂ as a Function of Reaction Time

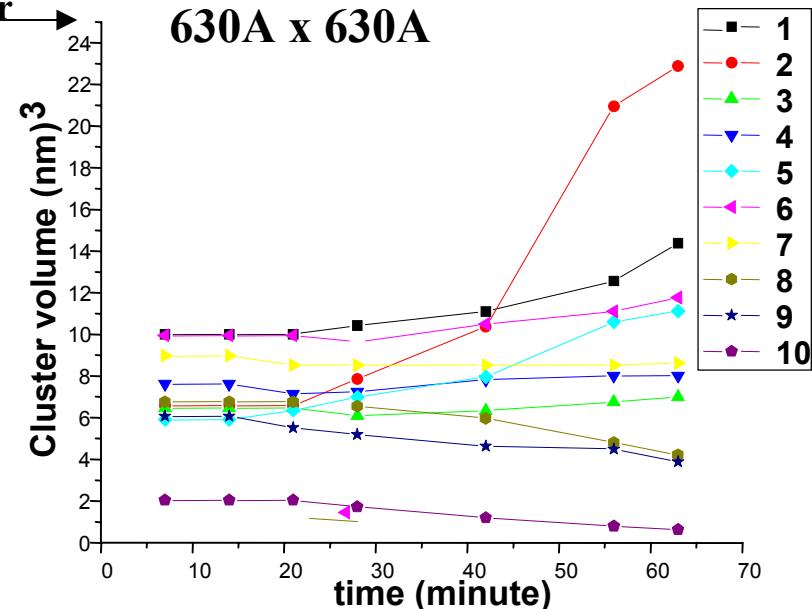
Reaction
Rate, CO₂
molecules
per site per
second



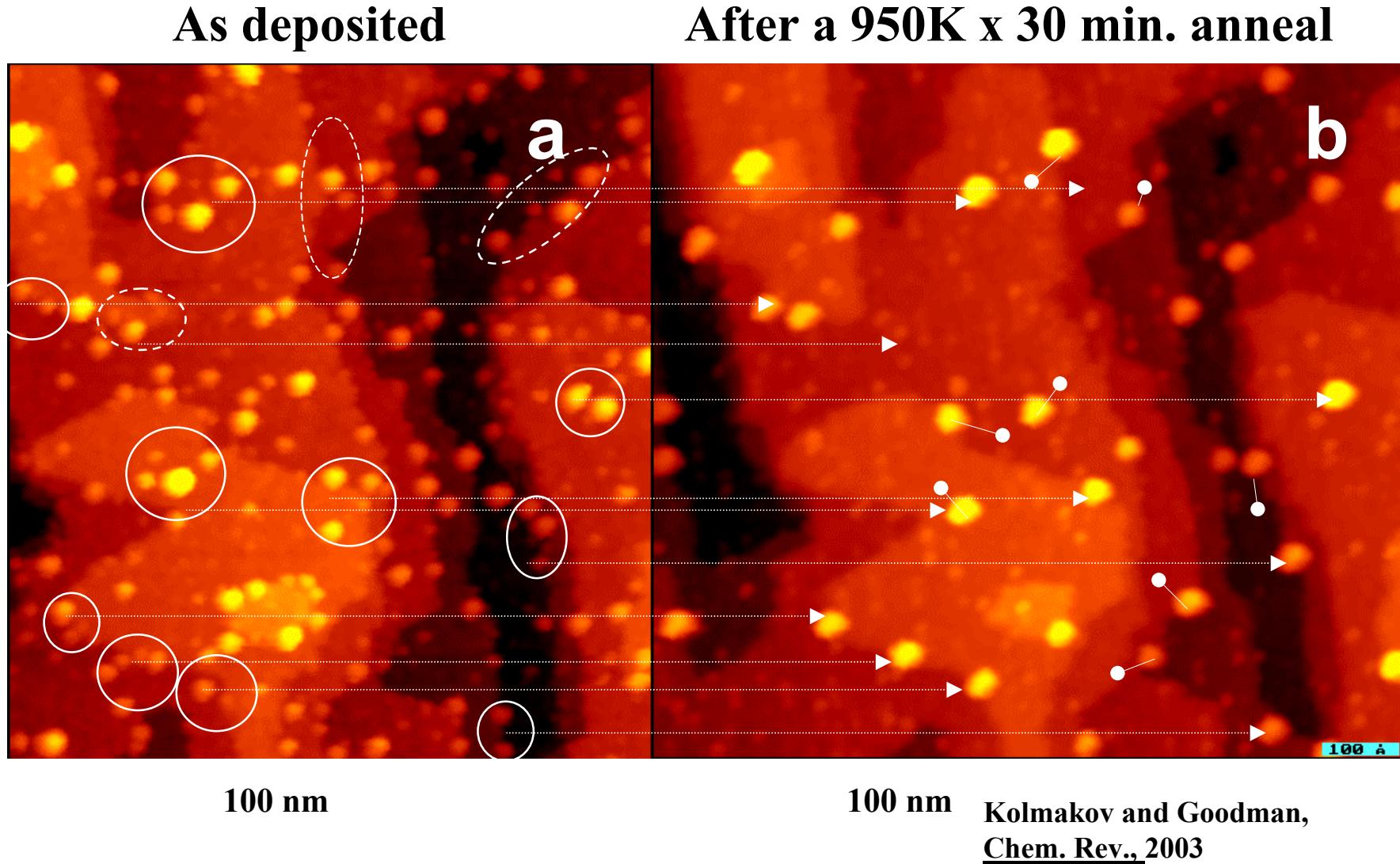
STM: 0.5 MLE Au/TiO₂(110), CO/O₂ (1:1), 4.2 Torr @ 420K



- Cluster size increase**
- Cluster size decrease**
- Cluster disappears**



Au/TiO₂(110) Before and After Annealing to 950K



Role of support in metal activation & cluster sintering:

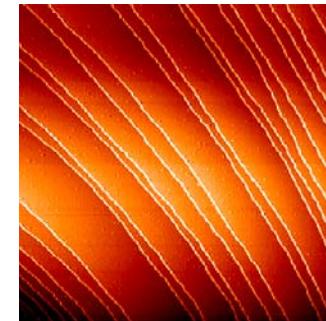
SiO_2 versus TiO_2 ?

Model Oxide-Supported Metal Catalysts

Thin Oxide Film Support + Metal Clusters

e.g. Mo, Re
Ta, W

Refractory Single Crystal

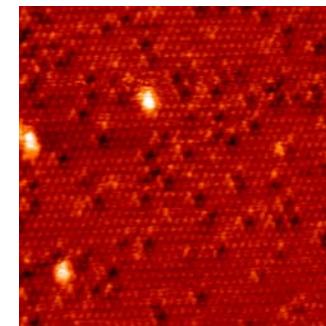


Mo(112)

e.g. SiO_2 , Al_2O_3 ,
 MgO , TiO_2
1-10 nm

Oxide Thin Film

Refractory Single Crystal

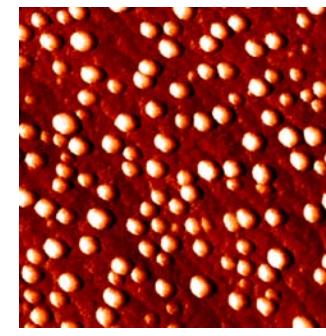


$\text{SiO}_2/$
Mo(112)

Metal Clusters
1.0 - 50 nm

Oxide Thin Film

Refractory Single Crystal

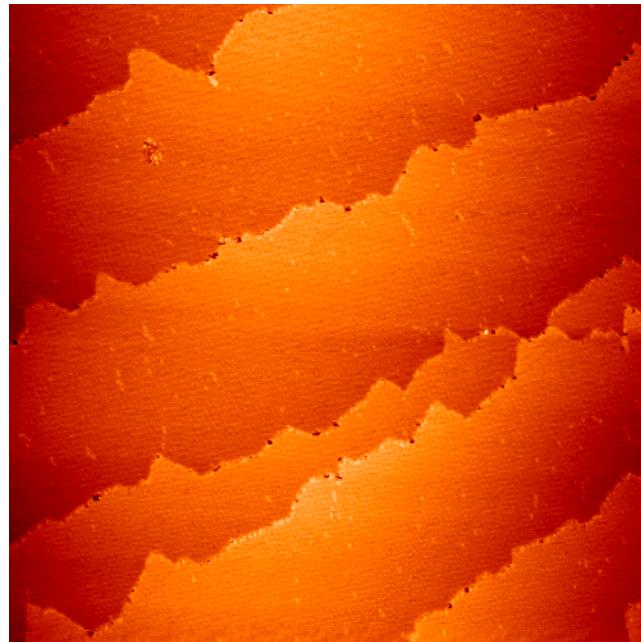


0.5 ML Au
 $\text{SiO}_2/$
Mo(112)

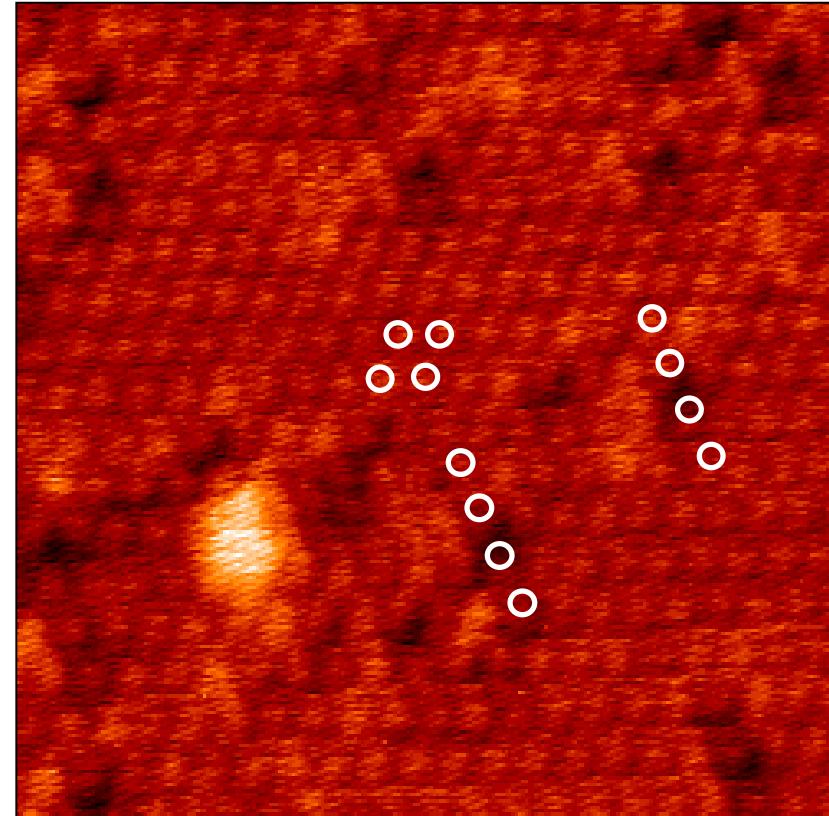
Preparation & Characterization of Ultra-thin, Well-ordered SiO₂/Mo(112)

Schroeder, Adelt, Richter, Naschitzki, Baumer, and Freund. *Surf. Rev. Lett.* 7 (2000)

1. Si @RT
2. O₂ @ 800K
3. Anneal @1200 K



400 nm

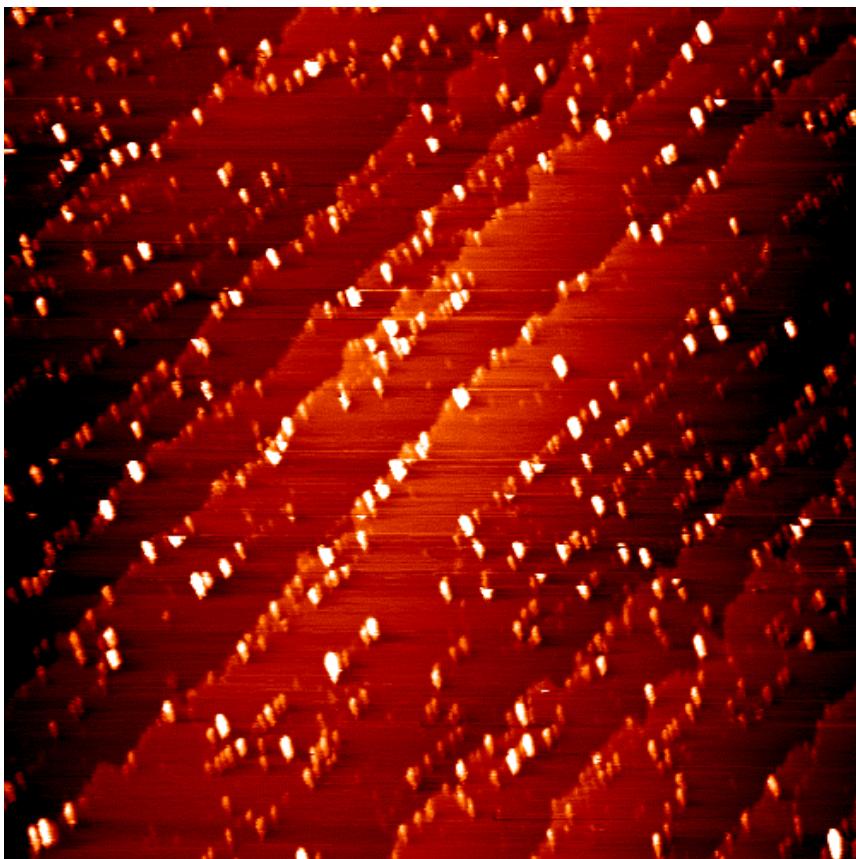


10 nm

0.7 nm thick, sharp hexagonal LEED with a band gap ~8.9 eV (STS)

Au Cluster Nucleation on Low-Defect Versus High-Defect SiO₂

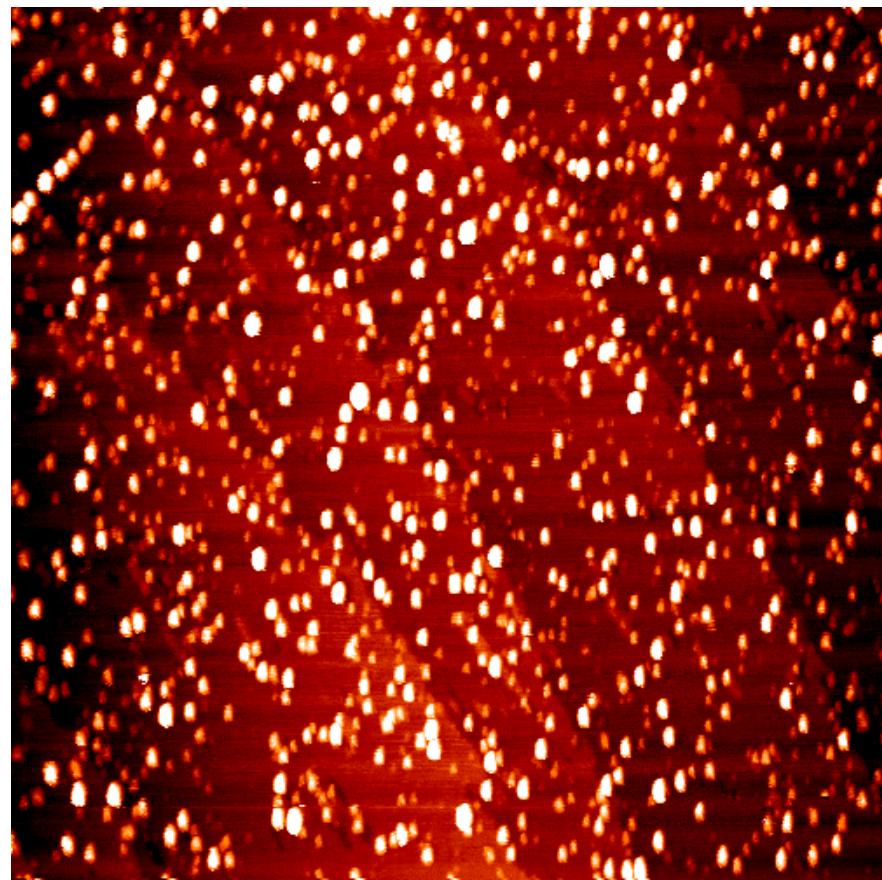
“Au + Low Defect SiO₂”



200 nm

0.40 ML of Au
0.033 ML/min
300 K

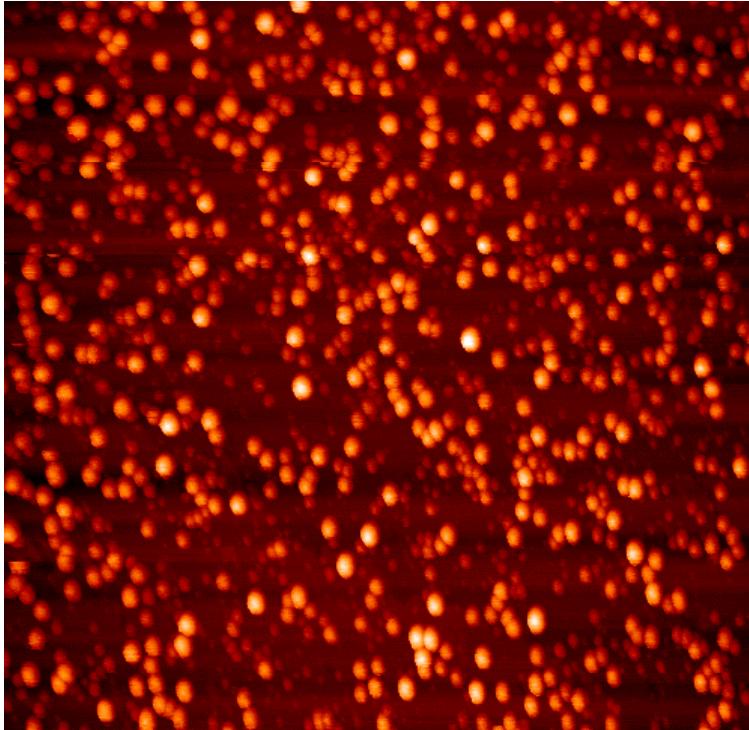
“Au + High Defect SiO₂”



200 nm

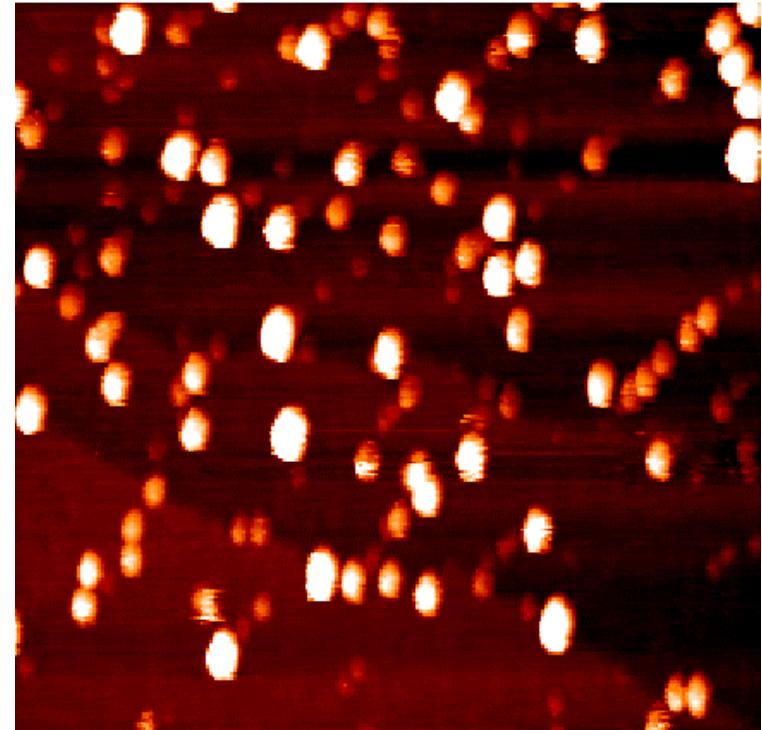
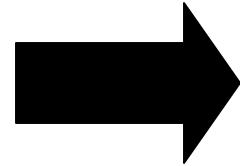
0.40 ML of Au
0.033 ML/min
300 K

Sintering of Au Clusters on SiO₂



200 nm

850 K
anneal

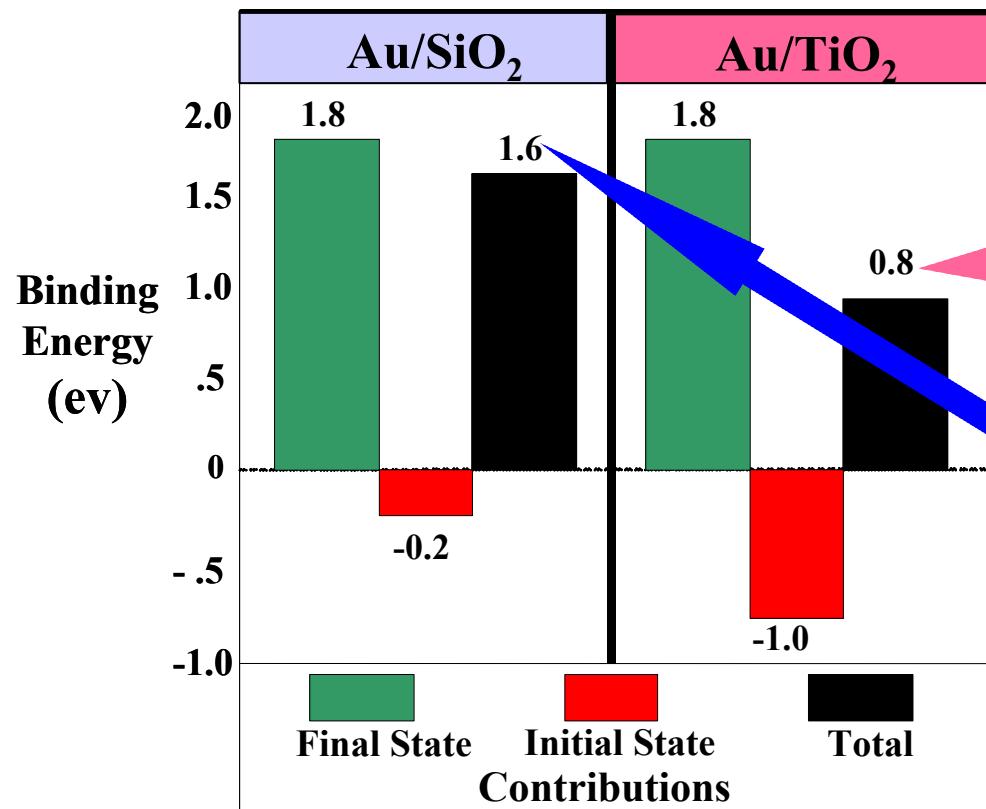


200 nm

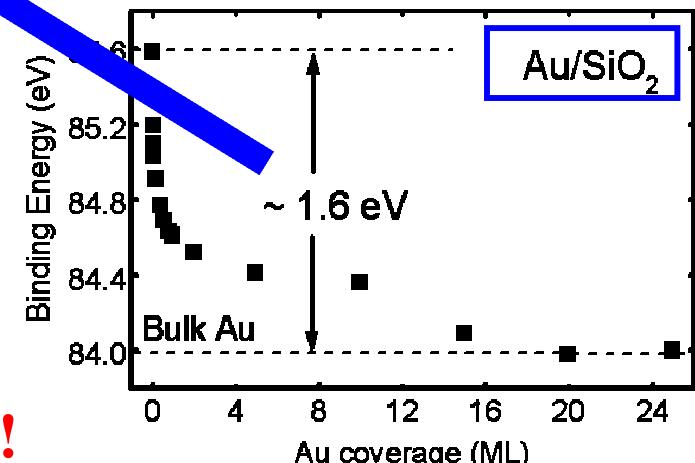
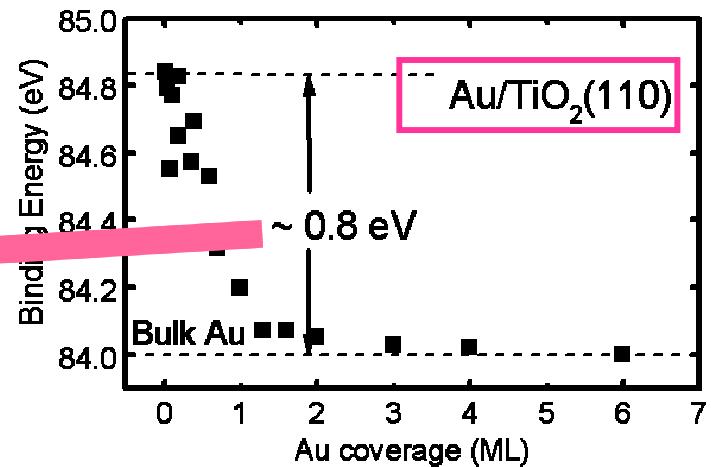
- Sintering of Au on SiO₂ more facile than on TiO₂
i.e., Au binds less strongly to SiO₂ than to TiO₂

XPS Core Level Shifts: Au/SiO₂ vs. Au/TiO₂

Core Level Shift: Bulk – Small Cluster Limit

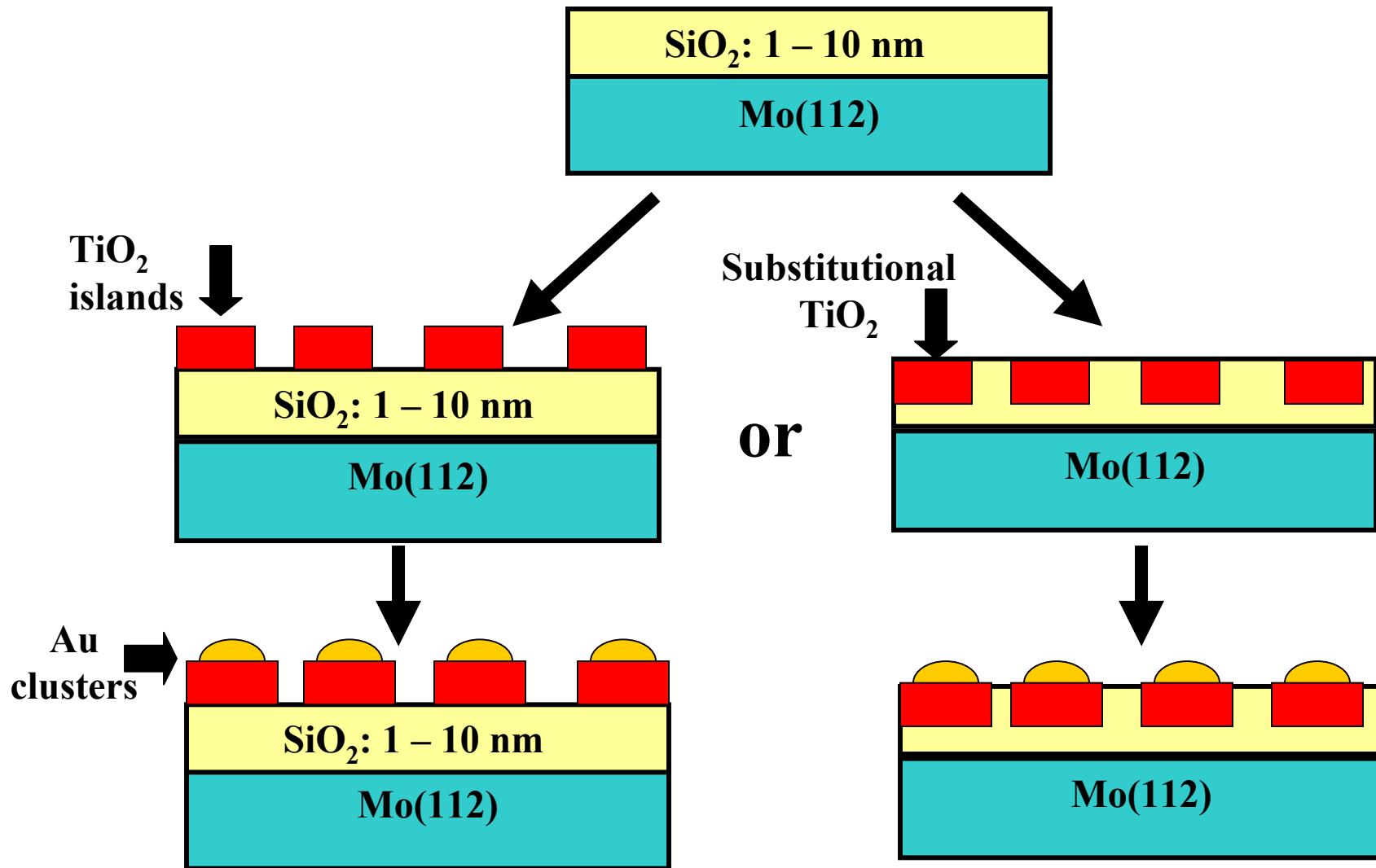


XPS Core Level Shifts



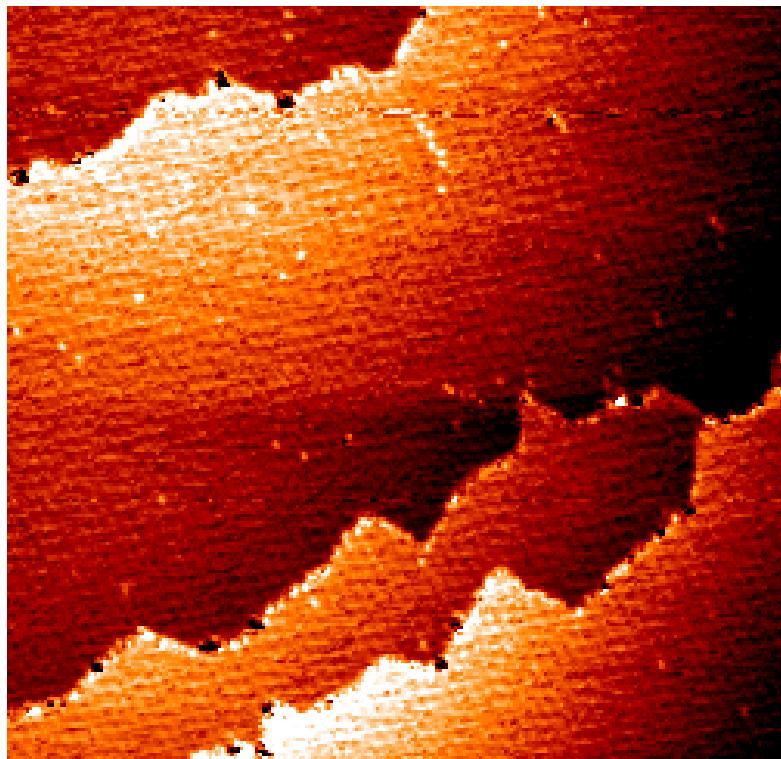
Implications: electron-rich Au on TiO₂!

Strategies for a Sinter-Resistant Support: TiO_2 Dispersed onto and into SiO_2



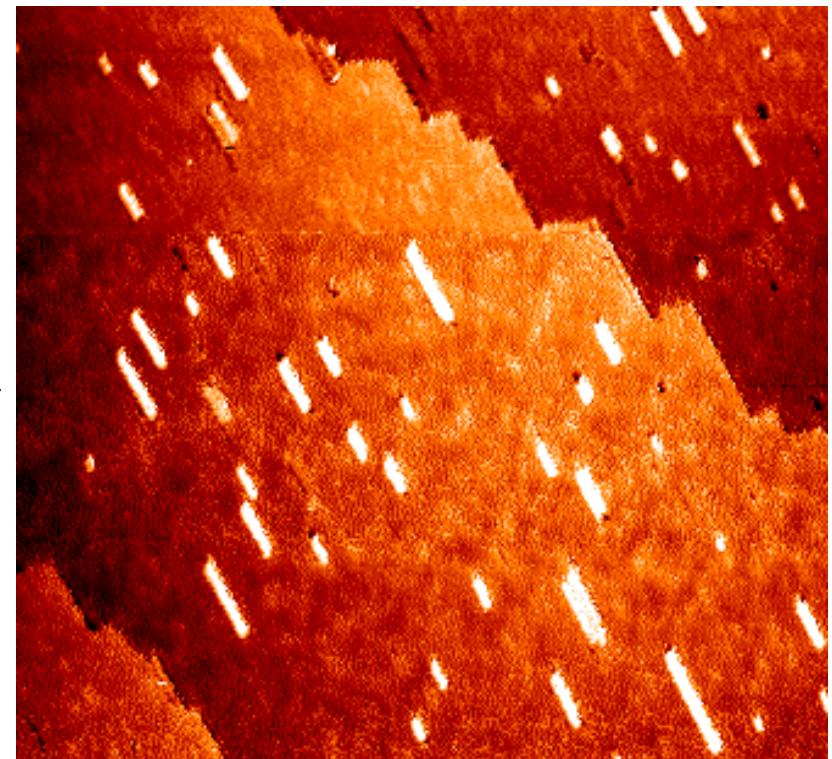
TiO_x Islands Dispersed on SiO_2

1.0 ML $\text{SiO}_2/\text{Mo}(112)$



100 nm

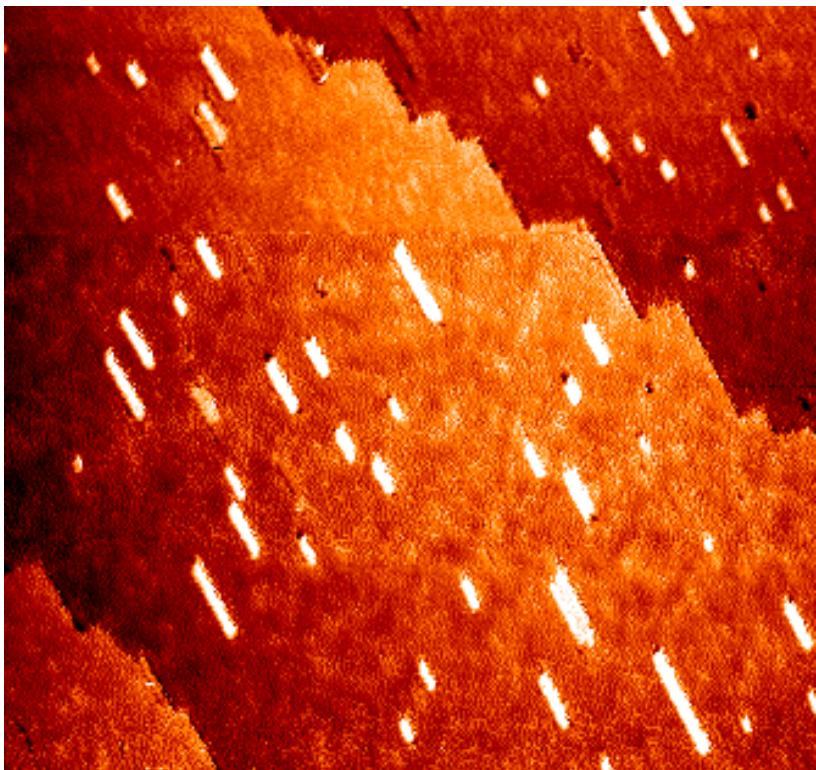
0.1 ML $\text{TiO}_x/\text{SiO}_2/\text{Mo}(112)$



100 nm

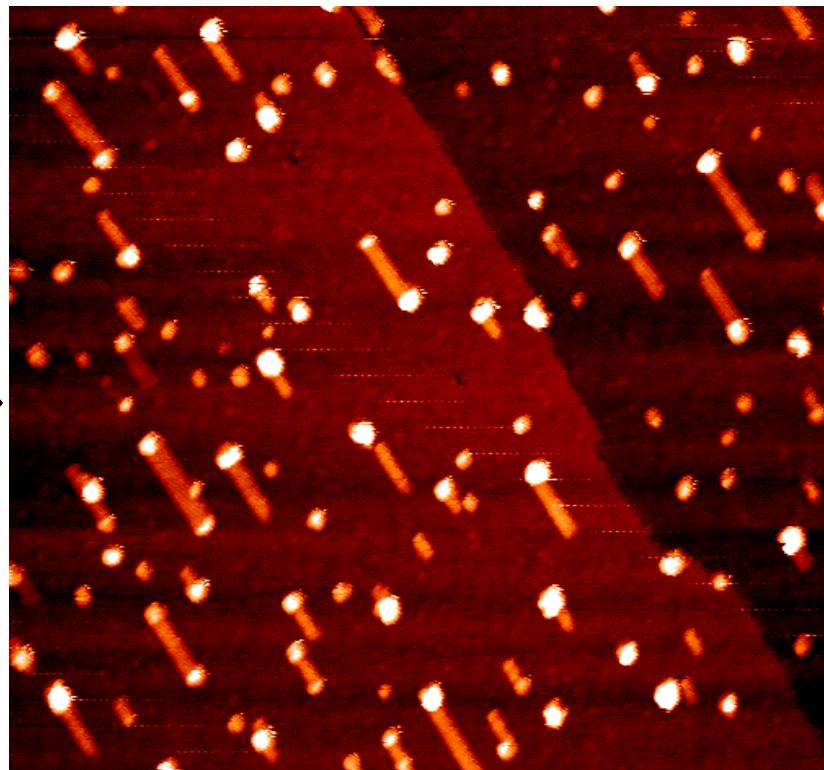
Au Particles Deposited onto TiO_x Islands Dispersed on SiO_2

0.1 ML $\text{TiO}_x/\text{SiO}_2/\text{Mo}(112)$



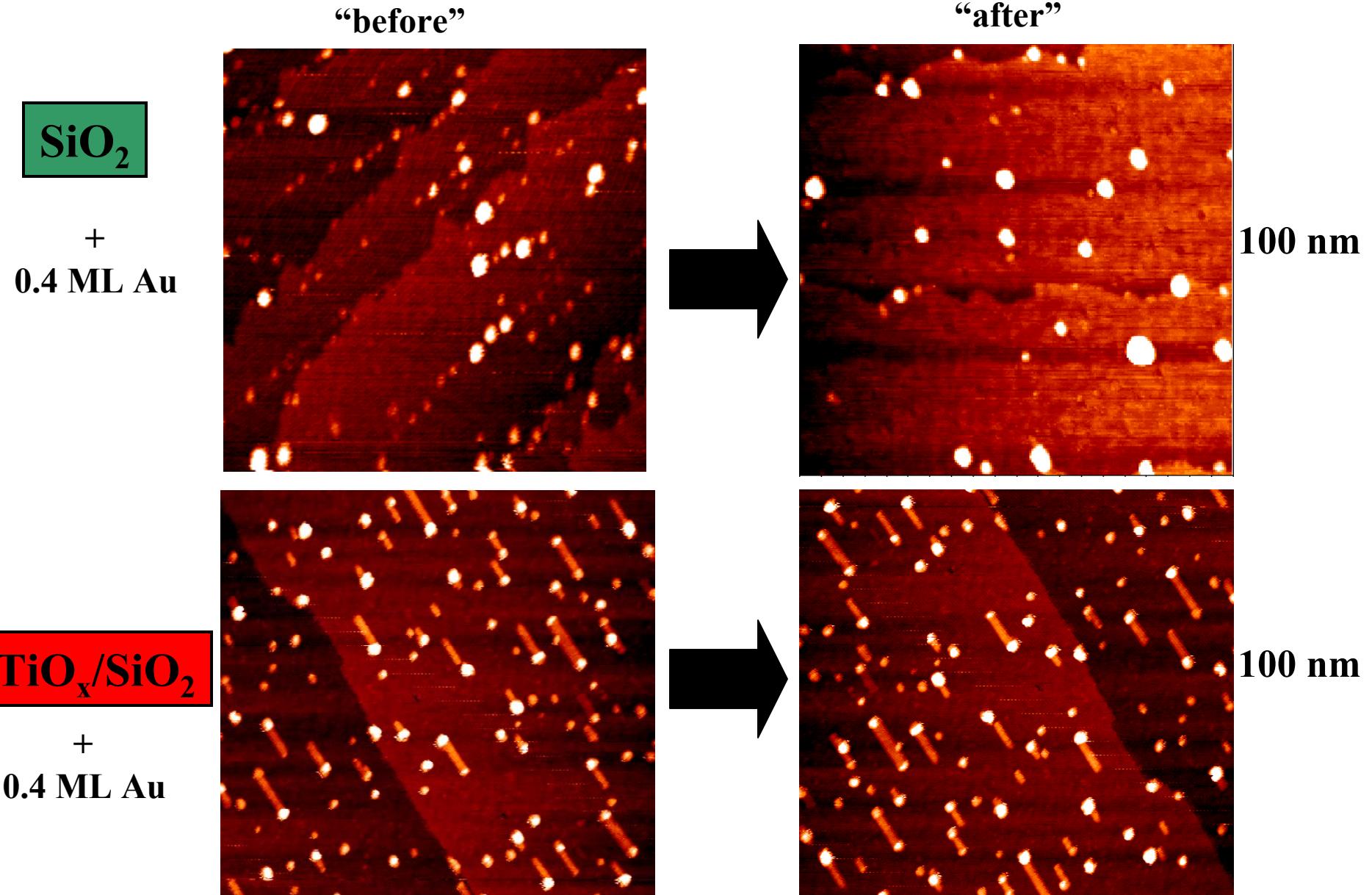
← 100 nm →

0.4 ML Au/ $\text{TiO}_x/\text{SiO}_2/\text{Mo}(112)$



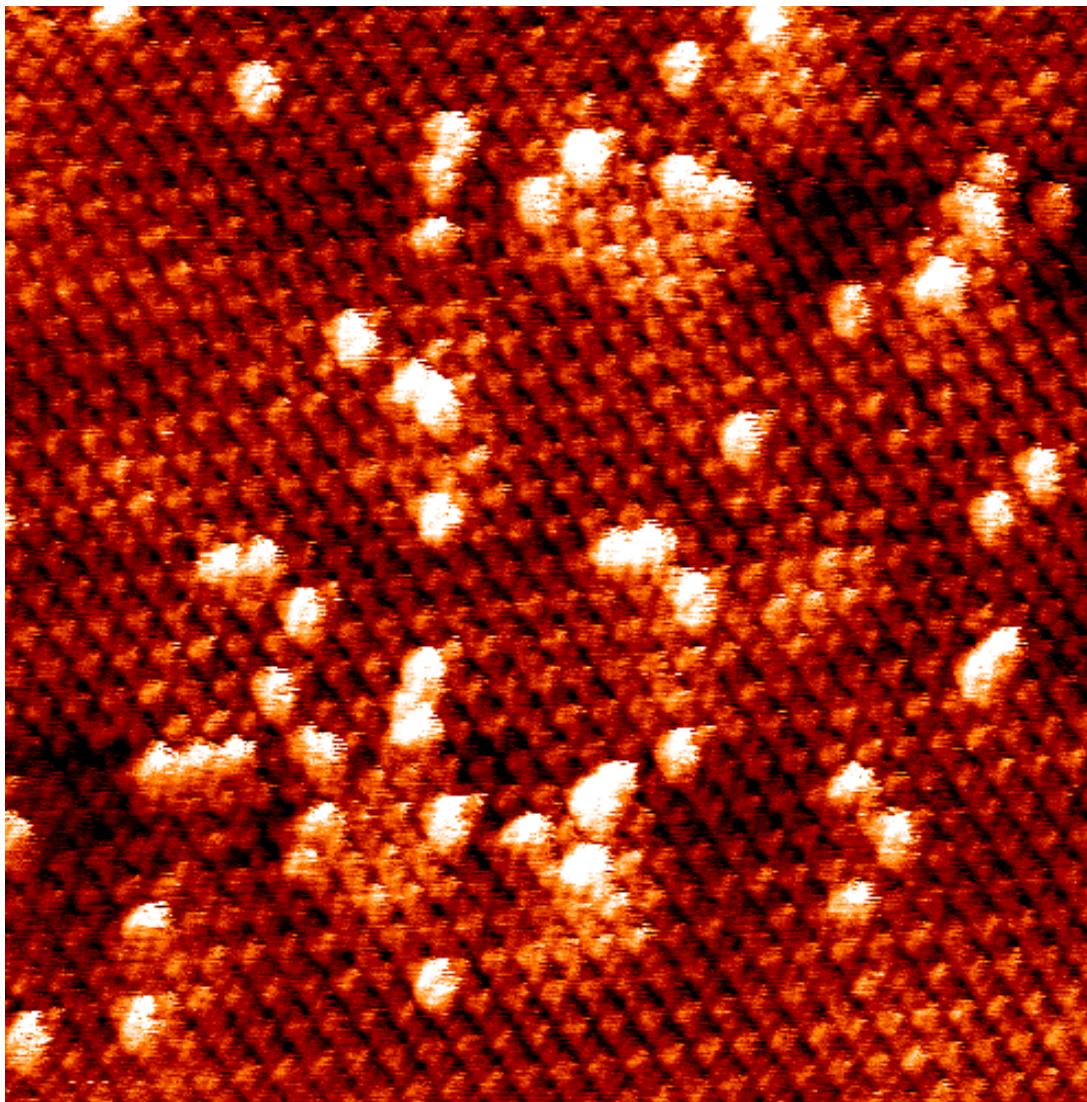
← 100 nm →

Au/SiO₂ versus Au/TiO_x/SiO₂: 850 K Anneal



Ti Point Defects on SiO₂

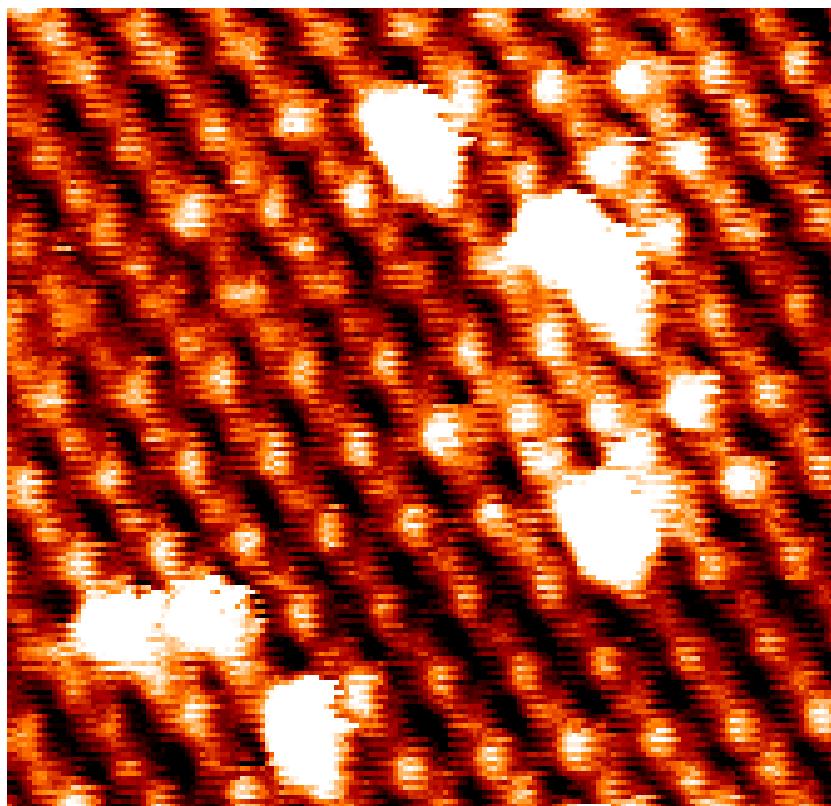
15 nm



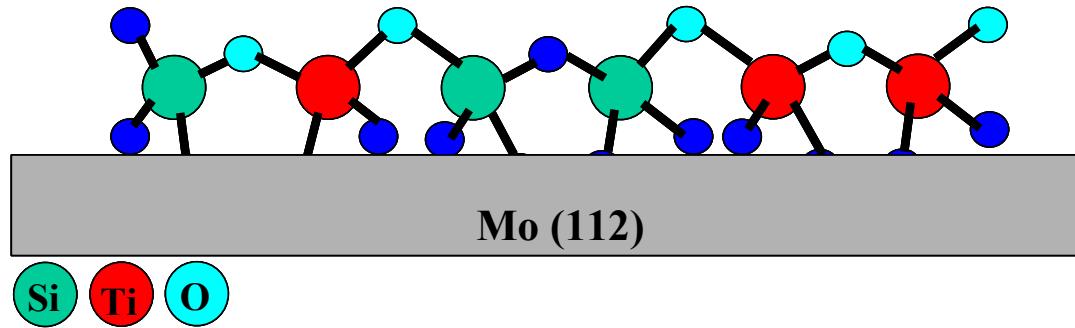
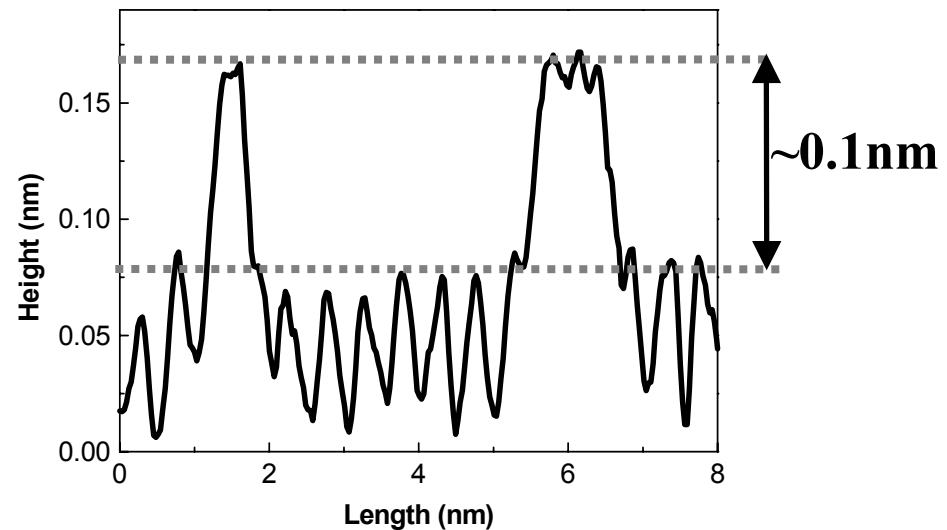
15 nm

STM: $\text{TiO}_x\text{-SiO}_2$ Thin Film with 2% Ti

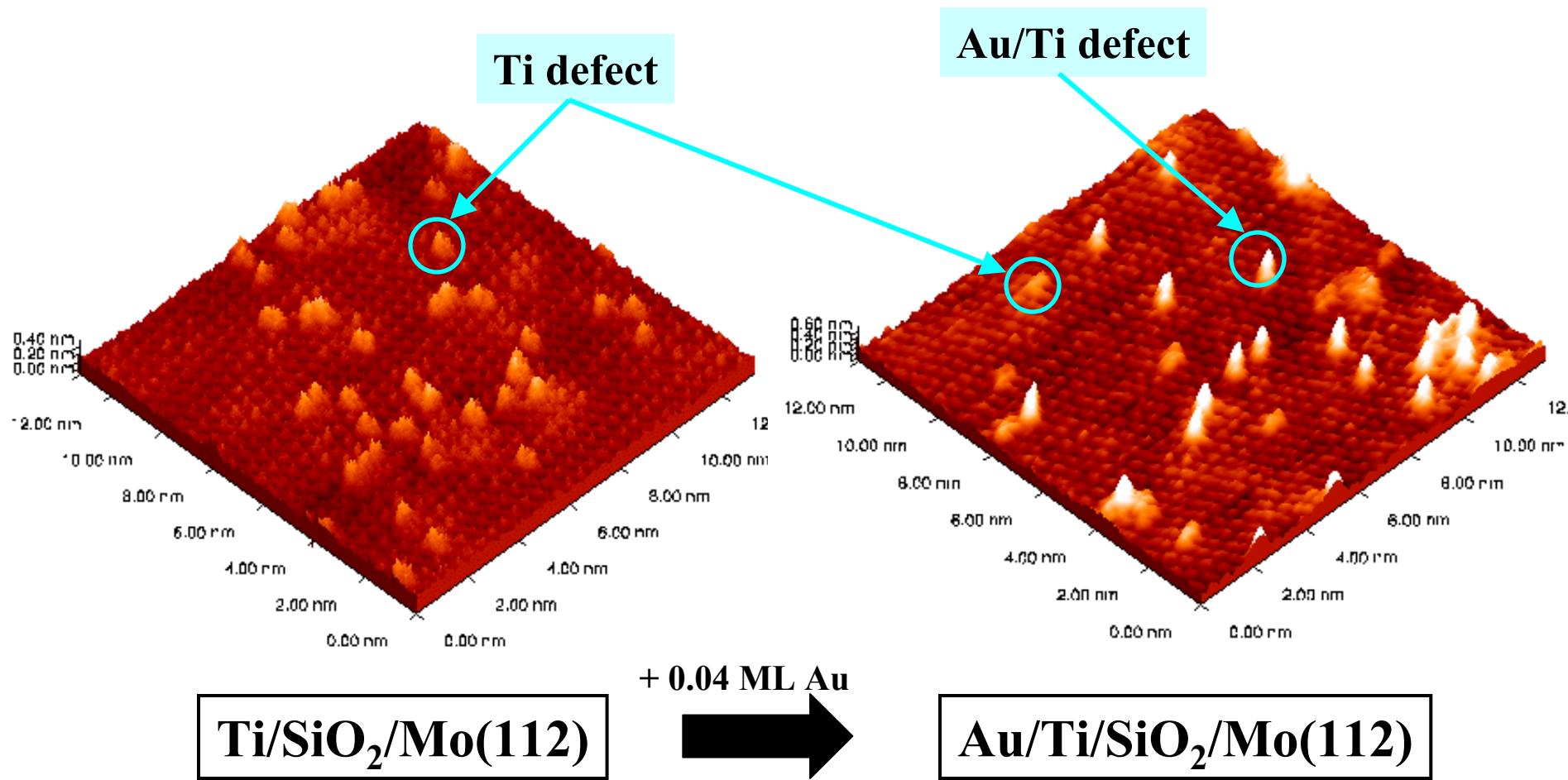
← 2.4 nm →



Scan across Ti defects



Decoration of Ti Point Defects with Gold



Question: How have neutrons aided our understanding of catalysis by metal nanoclusters?

Answer: INS, i. e., nature of surface intermediates on high surface area catalysts at realistic conditions!!

“The Nature of the Surface Species Formed on Au/TiO₂ during the Reaction of H₂ and O₂: An Inelastic Neutron Scattering Study”, C. Sivadinarayana, T. V. Choudhary, L. L. Daemen, J. Eckert and D. W. Goodman, J. Amer. Chem. Soc., 126, 38-39 (2004).

“Characterization of C₂(C_xH_y) Intermediates from Adsorption and Decomposition of Methane on Supported Metal Catalysts by In-Situ Inelastic Neutron Scattering Vibrational Spectroscopy”, C. Sivadinarayana, T. V. Choudhary, L. L. Daemen, J. Eckert and D. W. Goodman, Angewandte Chemie, 41, 144-146 (2002).

Conclusions

- Catalytic reactivity and selectivity are markedly different for clusters $< \sim 3.0$ nm.
- Core-level shifts, valence band structure, sublimation energies, and adsorbate binding energies are unique for clusters $< \sim 3.0$ nm.
- Nanoclusters are generally unstable to reaction conditions, i.e., understanding and maintaining stability are the keys to technological breakthroughs.

Coworkers

STM

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MIES

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Juergen Eckert (LANL)
Zhen Yan
Yi-Fan Han

IRAS

Jinhai Wang

XPS/ISS

Dheeraj Kumar

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